CHAPTER 1

INTRODUCTION

1.1 Project Background

Based the case-study from Engen Refinery, MDEA is run at 40% concentration for the Amines System. The MDEA is mainly used to scrub H_2S from the system. Once H_2S is absorbed, the amines go through the regenerator to scrub off the H_2S. The arising problems were that the amines were not absorbing enough H_2S. This problem was identified due to the high H_2S content in the fuel gas.

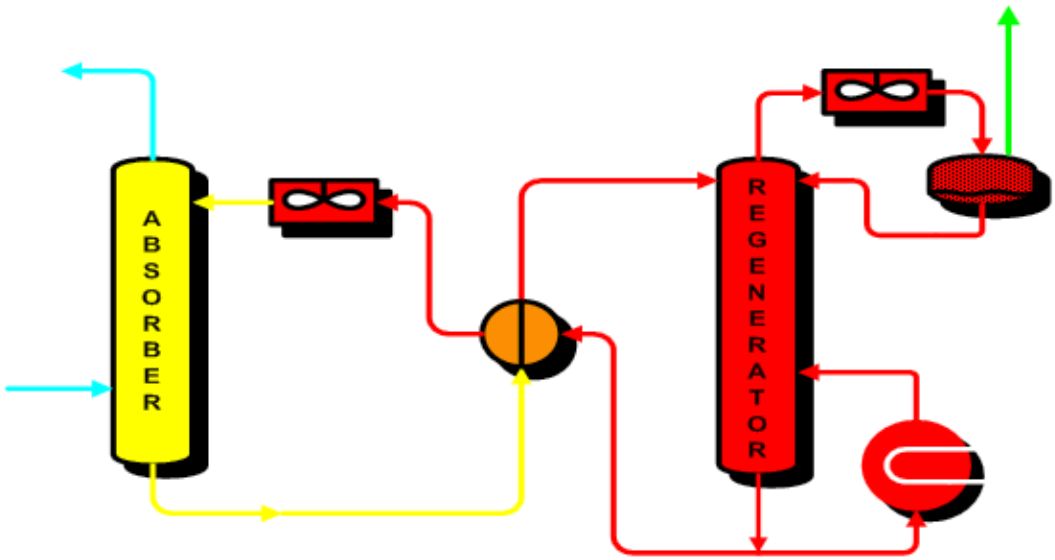

Figure 1: Basic amine gas sweetening system

The arising problems were that the amines were not absorbing enough H_2S. This problem was identified due to the high H_2S content in the fuel gas. The common problems with the amines are:

- High H_2S in fuel gas

- Limited scrubber capacity
- High amine losses/ Foaming
- Corrosion / Fouling/Heat Stable Salts (HSS)

The H_2S content, which was measured using parts per million, increased significantly as shown in the graph below:

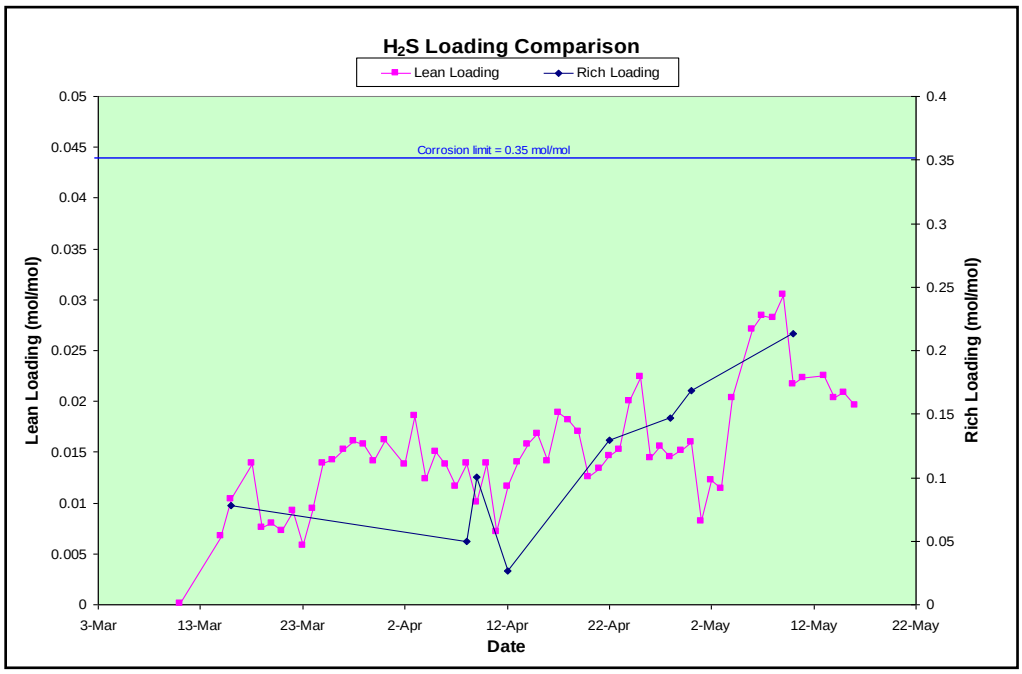

Figure 2: H_2S loading comparison between lean and rich amines

The amines circulation goes through a series of H_2S absorbers. HSS was suspected to degrade the amines ability to absorb H_2S. It causes the strength of amine to degrade causing the absorbers to be ineffective.

Analysis on amines is generally to determine the free amines in the system versus the total amines in the system. The free amines percentage is usually less than the total amines percentage because there's a percentage of amine that is bonded with the HSS. However, an analysis done on the free and total amines percentage shows that during the period where the H_2S content were high (Refer Figure 3), the free and total amine percentage were equal. This may be due to the overwhelming amount and

types of HSS in the system that it ceased forming with the amines itself. However, we don't have the mean to determine the actual reactions that occur in the solution.The graph below shows the difference between the strength of free amines versus the total amines in the system:

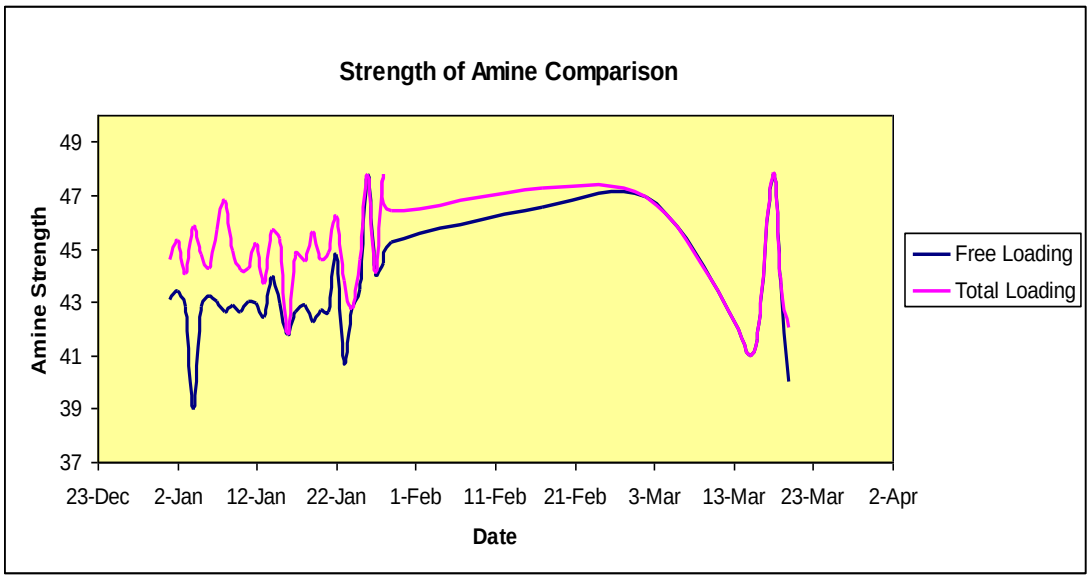

Figure 3: Strength of amines comparison graph

A trend was discovered between the lean loading and H_2S in fuel gas. A small increase in the loading would cause the H_2S in fuel gas to increase significantly.

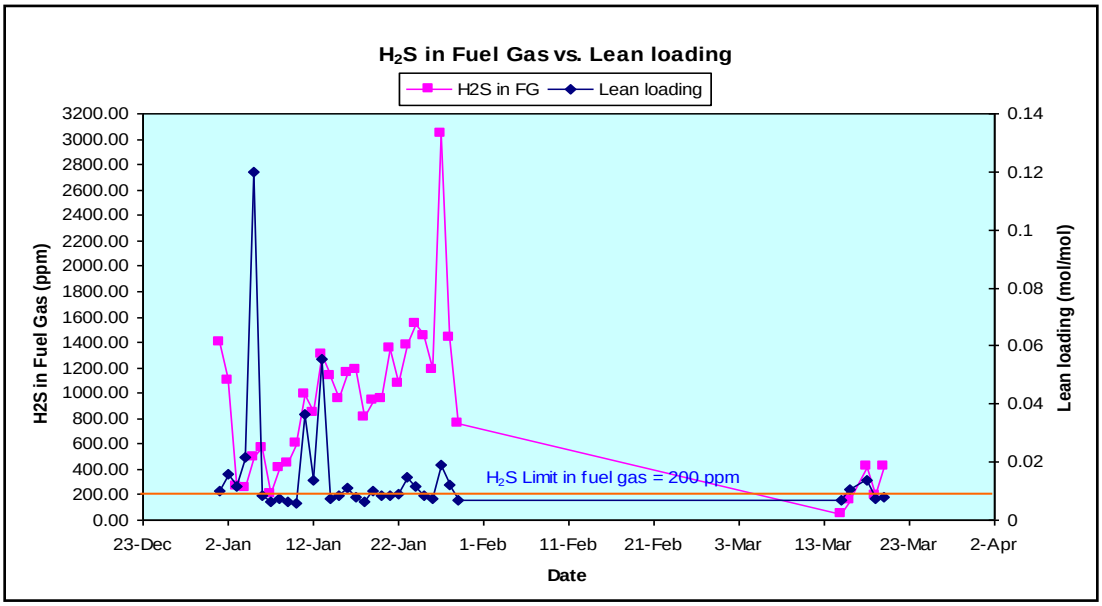

Figure 4: Correlation of H_2S in fuel gas and the lean loading

The source of the HSS in the No. 2 amine system is the FCCU/USGP plant:

- Hydrochloric acid, HCl
- Ammonium chloride, NH_4Cl
- Hydrogen sulphide, H_2S
- Ammonium hydrogen sulphide, NH_4HS
- Hydrogen cyanide, HCN
- Carbon dioxide, CO_2

Some other component such as Ni comes from the FCC feed. The dry gas to the amine absorber was how all these salts and contaminants leaks into the amine system (Refer Appendix I). A water wash system was established to resolve this problem. Other sources of chemicals in the No. 2 Amines system are from the anti-foaming agent.

1.2 Problem statement

An experiment was conducted using the waste or rich MDEA from the No. 2 amines system for neutralization with both KOH and Na_2CO_3. The solution had to first be filtrated due to presence of iron sulfide because of pipeline corrosion which is caused by the high acidity of the amine due to presence of excess HSS.

The selectivity of the solution is hard to be determined since the first endpoint of titration neutralizes the H_2S in the solution first. Due to many contaminants in the system, it is unclear as to which salts were neutralized and what precipitate were formed after the neutralization of the rich amine.

For this project, a closer study is to be done on the effect of neutralization of HSS in MDEA by using caustic as carbonate just adds the amount of carbamate which is very corrosive to the system. To study the effect of neutralization with caustic to MDEA characteristics, a model MDEA that is contaminated by acid contaminants that is present

the most in an amine system according to the data in Appendix 1 would be used to replace the rich amine. The byproducts could then be singled out and studied.

Furthermore, no research has been done specifically to observe the effect of HSS on different strengths of amine that is feasibly applicable in a plant the limit of which is from 20-55 wt%. This would help understand the tradeoff between cost savings and the optimum strength (in wt%) amine that should be used in a standard amine gas sweetening plant.

Figure 5: Contaminated amine before filtration

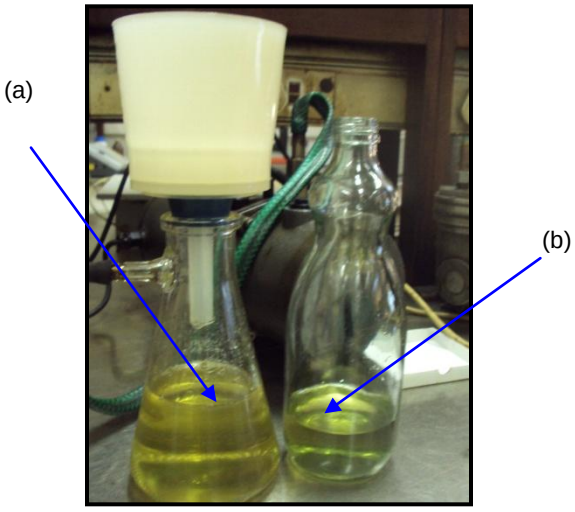

Figure 6: Comparison between amines 2 after (a) vacuum filtration and (b) kinematic filtration

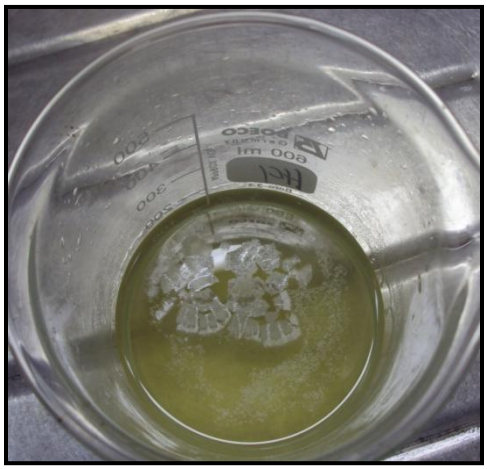

Figure 7: White precipitation appearing in the solution

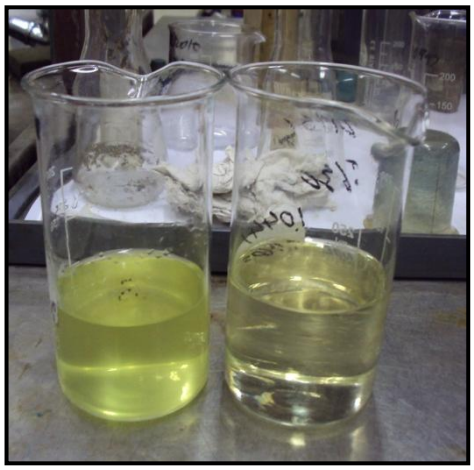

Figure 8: Comparison of color between fresh MDEA and 10 ml MDEA + 40ml KOH

1.3 Objectives and Scope of Study

The objectives and scope of study are:

1. To study the by-product formation (if any) and potential harm it may cause to the MDEA characteristics (E.g.: strength, quality, acid gas absorbency) at different strengths of amine.
2. To determine the MDEA characteristics after caustic is added and provide qualitative measure of HSS contamination
3. To determine the feasibility of adding caustic to neutralise MDEA is applicable to Amines system in the refinery

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of amines

Amines is a class of organic compounds of nitrogen that may be considered as derivation of ammonia (NH_3) by replacing one or more of the hydrogen atoms with alkyl groups. The amine is primary (MEA), secondary (DEA), or tertiary (MDEA) depending on whether one, two, or three of the hydrogen atoms are replaced. All amines are basic in nature and usually combine readily with hydrochloric or other strong acids to form salts [1].

For primary amines, only one of the hydrogen atoms in the ammonia molecule has been replaced. The formula of the primary amine will be RNH_2 where "R" is an alkyl group. For secondary amines, two of the hydrogen molecules in an ammonia molecule have been replaced by hydrocarbon groups. In a tertiary amine, all of the hydrogen molecules in an ammonia molecule have been replaced by hydrocarbon groups [2].

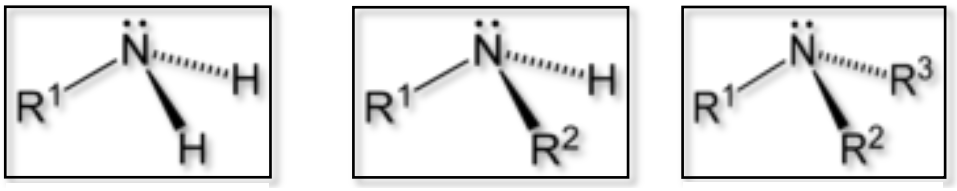

Figure 9: (a) Primary amines molecules, (b) Secondary amines molecules, (c) Tertiary amines molecules

2.2 Heat stable salt (HSS) contaminants

Heat stable salts (HSS) formation in amine solutions has been a problem for a long time especially in refinery systems or when oxygen or carbon monoxide is present in the feed gas to the amine unit. [17]

In a gas sweetening plant, there are 5 well-known types of amine contaminants [6, 7]:

- Heat stable salts
- Degradation
- Injection of chemicals
- Hydrocarbons
- Particulates

All of these contaminants typically can be present in any given amine system simultaneously, although the amount of each one can vary from inconsequential to several per cent.

For this particular project, the heat stable salts (HSS) effect towards the amine is proposed to be studied. HSS is made up of amine salts such as formate, acetate, glycolate, glyoxalate, oxalate, thiocyanate, thiosulfate, sulfate, sulfite and chloride which decrease the acid gas carrying capacity of the amine and increase solution viscosity which can increase foaming tendencies of the amine. Furthermore, HSS are also considered corrosive and this can lead to degradation in the amine pipe line thus increasing amine unit operating costs for constant maintenance. [7,17].

2.3 Current method of removing contaminants in the industry

There are several methods of handling contaminated amine systems. Depending on the type of contaminant, one or more of the following methods can be used for cleaning an amine system such as [7]:

- Disposal and Replace
- Continuous Disposal and Replace (Bleed and Feed)
- Filtration of Particulates
- Neutralization of Heat Stable Salts

- Electrodialysis
- Ion exchange
- Vacuum Distillation Reclaiming

Heat Stable Salts can be neutralized, usually with sodium/potassium hydroxide, which will free up the amine bound to the HSS anion. However, neutralization only changes the HSS from an amine HSS to a sodium/pottasium HSS, but does not remove any contaminants from the system.

According to literatures, this method could extend the time before having to reclaim or discard an amine solution. An aqueous sodium hydroxide (caustic) or aqueous potassium carbonate are extensively used in the gas treating industry to neutralize HSS. This is because these bases, being stronger bases than amines will react with the amine HSS to displace the amine and form the corresponding sodium or potassium salt, such as sodium or potassium salts of acetate, formate, oxalate etc. This displacement would then regenerate free amine to be used for acid gas absorption. [17]

Although neutralization of HSS with caustic does extend the time before the amine solution must be reclaimed or discarded, such neutralization still results in the formation of a number of solids in the amine solution. These solids are harmful to the operation of the amine solution and would lead to amine solution losses, increased maintenance activities and occasionally – plant shutdowns. Therefore, it would be advantageous to reduce the amount of solids formed in the amine solution and/or the useful life of the amine solution is increased while applying neutralization of amine solutions containing HSS.

2.4 Amines utilization in the industry

Amines are used in many oil refineries to remove acid gases from liquid hydrocarbons such as liquefied petroleum gas (LPG).This process is called amines gas

treating or also known as gas sweetening. Amines gas treating removes acidic contamination from hydrocarbon streams including [6, 10]:

- Hydrogen Sulphide (H_2S)
- Carbon Dioxide (CO_2)
- Mercaptans (R-SH)

These compounds are referred to as “acid gases”. Amine gas treating refers to a group of processes that use aqueous solutions of various amines to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from gases. The most commonly used amines in industrial plants are the alkanolamines used to be MEA and DEA. These days, MDEA is more favorable.

The acid gases to be removed are H_2S for this project. However, CO_2 is also available in the system which is essentially a neutral compound. In most cases is removed via the formation of carbonic acid, which is a kinetically slow process and may need to be catalyzed by the interaction of a carbamate though carbamate is said to be a very corrosive compound. H_2S is much more reactive and is easier to remove. This is due to the fact that it may be better to use this higher reactivity to consider as an alternative to wash processes for the removal of H_2S [3].

The amine concentration in the absorbent aqueous solution is an important parameter in the design and operation of an amine gas treating process. Depending on which one of the following four amines the unit was designed to use and what gases it was designed to remove, these are some typical amine concentrations, expressed as weight percent of pure amine in the aqueous solution [10]:

- Monoethanolamine: About 20 % for removing H_2S and CO_2, and about 32 % for removing only CO_2.

- Diethanolamine: About 20 to 25 % for removing H_2S and CO_2

- Methyldiethanolamine: About 30 to 55% % for removing H_2S and CO_2
- Diglycolamine: About 50 % for removing H_2S and CO_2

The choice of amine concentration in the circulating aqueous solution depends upon a number of factors and may be quite unclear. It is usually made simply on the basis of experience.

The first factor is to determine whether the amine unit is treating raw natural gas or petroleum refinery by-product gases that contain relatively low concentrations of both H_2S and CO_2 or whether the unit is treating gases with a very high percentage of CO_2 such as the off gas from the steam reforming process used in ammonia production or the flue gases from power plants.

Due to the fact that H_2S is an acid gas, therefore it is corrosive to carbon steel. The H_2S forms a film of iron sulfide on the surface of the steel that acts to protect the steel. However, this is an endless loop of corrosion as the more steel corroded, the more iron sulfide is formed and in consequence more particulates and H_2S would find itself recycled back into the system.

Another factor involved in choosing an amine concentration is the relative solubility of H_2S in the selected amine. The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either H_2S alone if desired [10].

Selective absorption is dependent on several process variables, some of which cannot be specified or controlled by the design engineer. The variables include absorber pressure, amine temperature, and concentration of acid gases, residuals in lean amine,

residence time and weight percentage of amine. Furthermore, each of these variables interacts to give a very complex system.

2.5 Choice of amine

According to literatures, for gas sweetening, one of the most significant advantages of the last twenty years has been the use of N-methyldiethanolamine (MDEA) in amine treaters. MDEA is most preferable as it is the only amine used for gas sweetening which is flexible enough for efficient use in both bulk acid gas (H_2S and CO_2) removal or selective H_2S scrubbing. [18]

The advantages of using MDEA over other amines are as the following:

- Higher absorption capability and selectivity for H_2S as compared with other amines.
- Increased acid gas scrubbing or sweetening capacity and lower circulation rates.
- Lower operating temperature equates to additional economies not available with alternative systems.
- The low foaming properties of MDEA proves to be the most cost-effective gas sweetening agent for a variety of conditions.
- MDEA does not react with CO_2 to form a stable carbamate.

2.6 Choice of caustic

The specific reaction in the project would be between a weak acid and a strong base. The weak acids to be analyzed in this project are formic acid and acetic acid. Formate and acetate is the contaminants in the amine system to be analyzed. Therefore, a suitable caustic must be chosen. The specific reaction in the project would be between a weak acid and a strong base.

A strong base must therefore be chosen to neutralize the weak acids listed.

Table 1: List of strong bases [16]

Strong Bases	The Formulae
Lithium hydroxide	LiOH
Sodium hydroxide	NaOH
Potassium hydroxide	KOH
Rubidium hydroxide	RbOH
Caesium hydroxide	CsOH
Barium hydroxide	$Ba(OH)_2$
Calcium hydroxide	$Ca(OH)_2$
Strontium hydroxide	$Sr(OH)_2$

A common practice in the industry is to use either sodium hydroxide (NaOH) or potassium hydroxide (KOH). As this study would incorporate the findings for feasibility of application in the plant, NaOH is not attractive as it might combine with CO_2 in the amine system to produce $NaCO_3$. It would further degrade to produce carbamate. Carbamate is a corrosive in an amine system. For this project, KOH is chosen.

The concentration of KOH used in the present process depends on the specific operating condition of a plant and/or the amount of contaminants. From literature, generally the KOH concentration is about 5 to about 60 weight percent. Preferably the potassium hydroxide concentration is about 25 to about 50 weight percent. More preferably the potassium hydroxide concentration is about 35 to about 50 weight percent. Lower concentrations can be used. However, for operating plants that cannot handle the extra water that enters the plant, some of the circulating amine solution may have to be removed to allow for the extra KOH solution required. [17]

CHAPTER 3

METHODOLOGY

3.1 Research methodology

Figure 10: Research methodology flow chart

3.2 Flow chart of experiment

The flow chart of the experiment is as the following:

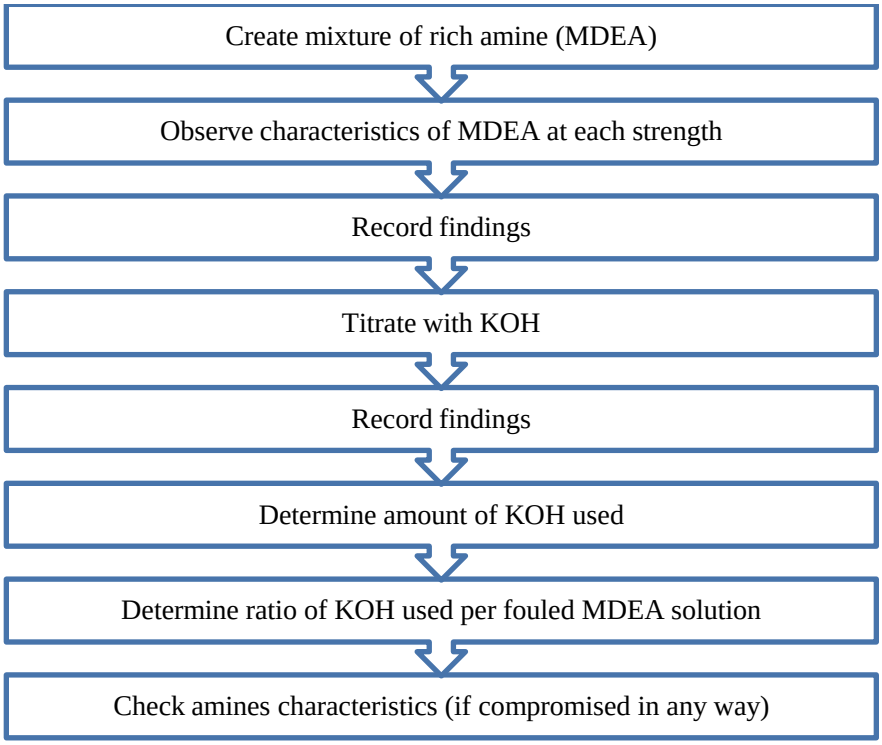

Figure 11: Project activities

3.3 Tools and Equipment

3.3.1 Chemicals

The chemicals required for this experiment are:

- MDEA solution
- KOH solution
- Formic acid
- Acetic acid

3.3.2 Apparatus

The apparatus required for this experiment are:

- Beakers
- Burette
- Conical flasks
- Volumetric flasks
- Retort stand
- Burette clamp
- Weight scale
- Eutech pH 510, pH meter

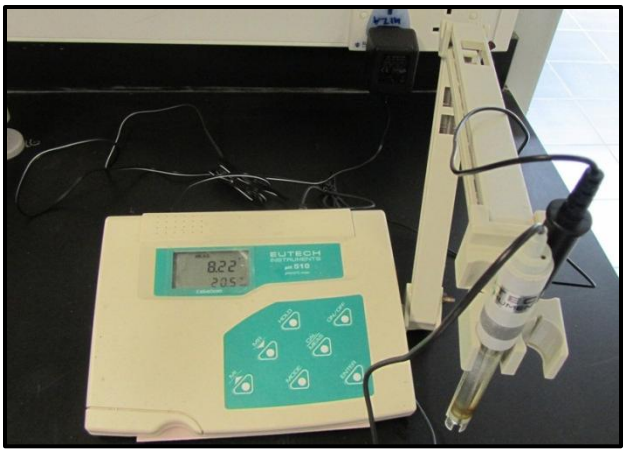

Figure 12: Eutech pH 510, pH meter

3.4 Procedures of the experiment

3.4.1 Preparation of dilute MDEA solution at different strengths

Procedures:

1. The amount of pure MDEA necessary to create a 30%, 40% and 50% strength wt% solution is determined using the formula below:

$$Weight\ Percent = \frac{Weight\ of\ solute}{Weight\ of\ solution}\ x\ 100\%$$

2. Dilute solution in a 100ml volumetric flask for each strength.

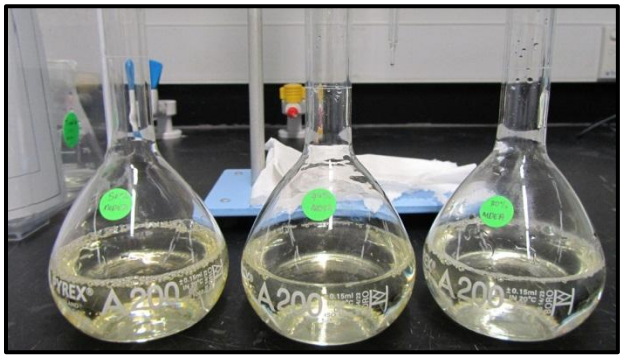

Figure 13: MDEA solution at different strengths

3.4.2 Determination of dilute KOH solution concentration

Procedures:

1. KOH solution is diluted to 0.4N.
2. The solution is titrated with a dummy contaminated MDEA solution.
3. pH of each solution is taken.
4. Record findings.
5. Repeat for next concentration to 0.9N by 0.1 intervals each.

6. Determine the most suitable solution to use for this the MDEA neutralization experiment.

3.4.3 Preparation of MDEA solution with acid contaminants

Procedures:

1. pH reading for the MDEA sample of each strength wt% (30%, 40% and 50%) is taken.
2. A 10 ml sample is taken.
3. The solution is then contaminated with 1ml of formic acid
4. Take pH of the solution
5. Record observation
6. Repeat steps 4-5 up of formic acid solution with the interval of 1ml and observe the MDEA degradation
7. Repeat steps 2-7 for MDEA strength of 40 and 50%
8. Repeat steps 1-8 for acetic acid

3.4.4 Addition of KOH to the contaminated MDEA solution

Procedures:

1. Contaminated amine is titrated with KOH one ml at a time.
2. pH reading is taken at every interval.
3. The titration is stopped when the pH of solution is the approximately the same as the solution before acid contamination which is about 12 for all strengths.

3.5 Calculation of TAN (Total Acid Number)

A tan test is to determine the acidity of a certain solution. Even though MDEA is a basic solution, the HSS contaminants in the system

have an acidic profile. It is expressed as the quantity of base (in this case mg of KOH) per grams of sample required to titrate a sample to its endpoint.

The total acid number is calculated as follows:

$$Total\ acid\ number, mg\ KOH/g = \frac{(A\ -\ B)\ x\ N\ x\ 56.1}{W}$$

Where:

A = Volume (cm^3) of alcoholic KOH solution used to titrate the sample to the endpoint

B = Volume (cm^3) of alcoholic KOH solution used for the blank titration.

N = Normality of the alcoholic KOH solution.

W = Mass of the sample in grams.

3.6 Gantt Chart

Project Activities	W1	W2	W3	W4	W5	W6	W7	W8	W9	W 10	W 11	W 12	W 13	W 14	W 15
Project Work Continues															
Progress Report Submission															
Pre-EDX															
Submission of draft report															
Submission of dissertation (soft bound)															
Submission of technical paper															
Oral Presentation															
Submission of dissertation (hard bound)															

Figure 14: Key Milestone of FYP 2

CHAPTER 4

RESULTS AND DISCUSSION

4.1 MDEA characteristics at different strengths after HSS addition

4.1.1 Degradation & Foaming of MDEA

The following graphs (Refer to Figure 18- Figure 22) represent the level of degradation of MDEA when polluted with contaminants.

For MDEA at 30% strength (wt %), the one polluted with formic acid loses its basic character when approximately 8ml of acid entered the solution. For the MDEA sample polluted with acetic acid, it retained the basicity of the solution until 10ml of the acid is added.

For MDEA at 40% strength (wt %), the one polluted with formic acid loses its basic character when approximately 10ml of acid entered the solution. For the MDEA sample polluted with acetic acid, it retained the basicity of the solution until 12ml of the acid is added. This solution showed foaming tendency after 7ml of acid was added to the system. The color of the solution turned from light yellow to a lighter color.

For MDEA at 50% strength (wt %), the one polluted with formic acid loses its basic character when approximately 6ml of acid entered the solution. For the MDEA sample polluted with acetic acid, it retained the basicity of the solution until 9ml of the acid is added. This solution showed foaming tendency after 1ml of acid was added to the system. The color of the solution turned from light yellow to a clear color with white precipitate formation.

From the experiment conducted, it shows that the level of degradation of the solution is more when it is reacted with formic acid. From literatures, a common strength of amine utilized in the industry is between 25 – 55 %.

However, through this experiment, results shows that although a 50% MDEA strength (wt %) is stronger than any other MDEA used, it is shown that the solution reacts more with MDEA as level of degradation is consistent when observed with two different contaminants which are acetic acid and formic acid (Figure 8 and 9). There is also rapid formation of visible solids (formate salt) at this strength.

Foaming tendencies is also higher. For acetic acid, it is observed to be less harmful to the MDEA when compared to the formic acid. The optimum strength of MDEA from this experiment that can withstand degradation is the one with 40% strength.

For MDEA at 30% strength (wt %), the solution has very slight foaming tendencies at this strength even though it is polluted with contaminants. The color of the solution turned from light yellow to a lighter color. For MDEA at 40% strength (wt %), this solution showed foaming tendency after 7ml of acid was added to the system. The color of the solution turned from light yellow to a lighter color.

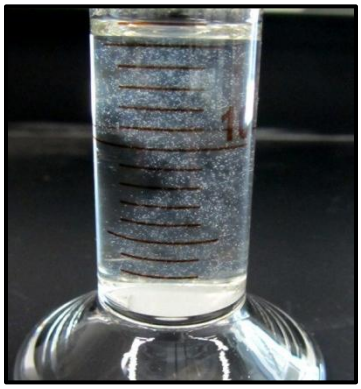

Figure 15: Suspended solids formed (HSS- formate)

Figure 16: Two layer of solution formed as acetate HSS settled

Figure 17: Foaming of the solution

The graphs are as below:

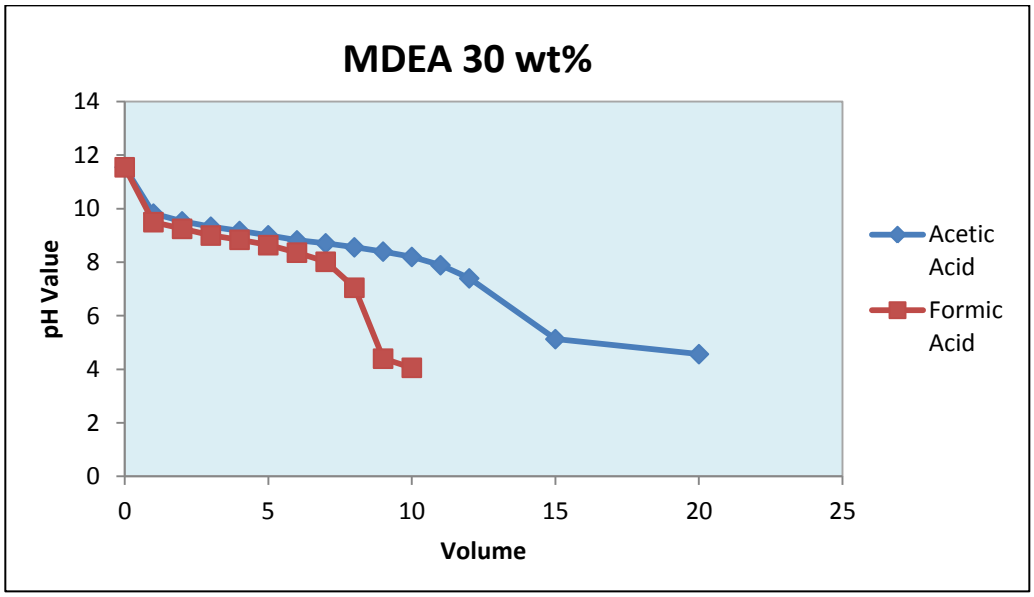

Figure 18: Comparison of acetic acid and formic acid contamination at 30% strength of MDEA

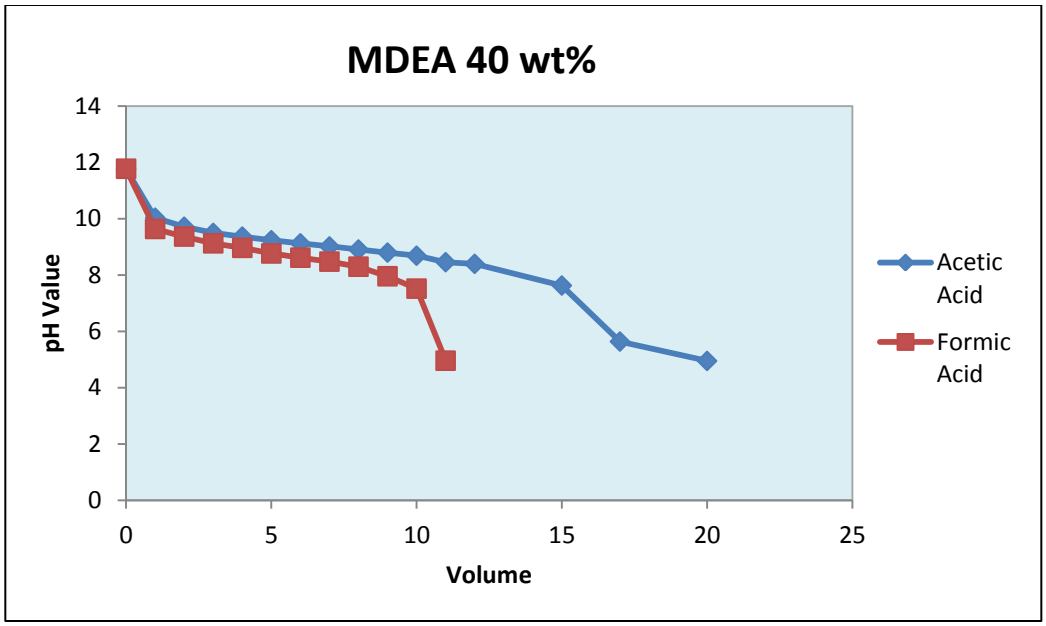

Figure 19: Comparison of acetic acid and formic acid contamination at 40% strength of MDEA

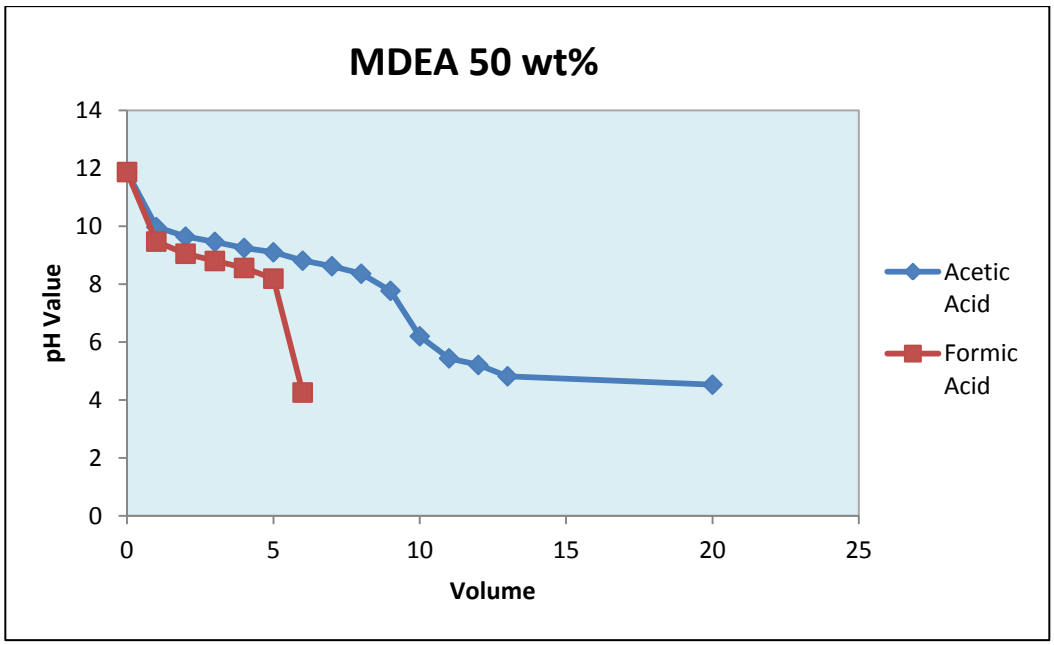

Figure 20: Comparison of acetic acid and formic acid contamination at 50% strength of MDEA

4.2 MDEA degradation profile comparison

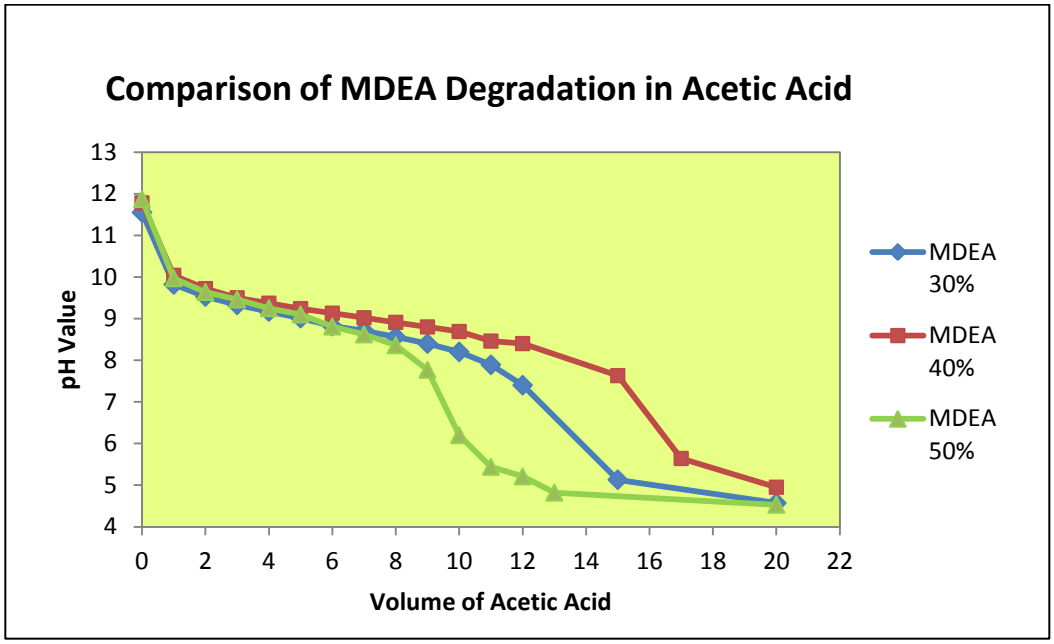

Figure 21: Comparison of MDEA degradation in acetic acid at different strengths

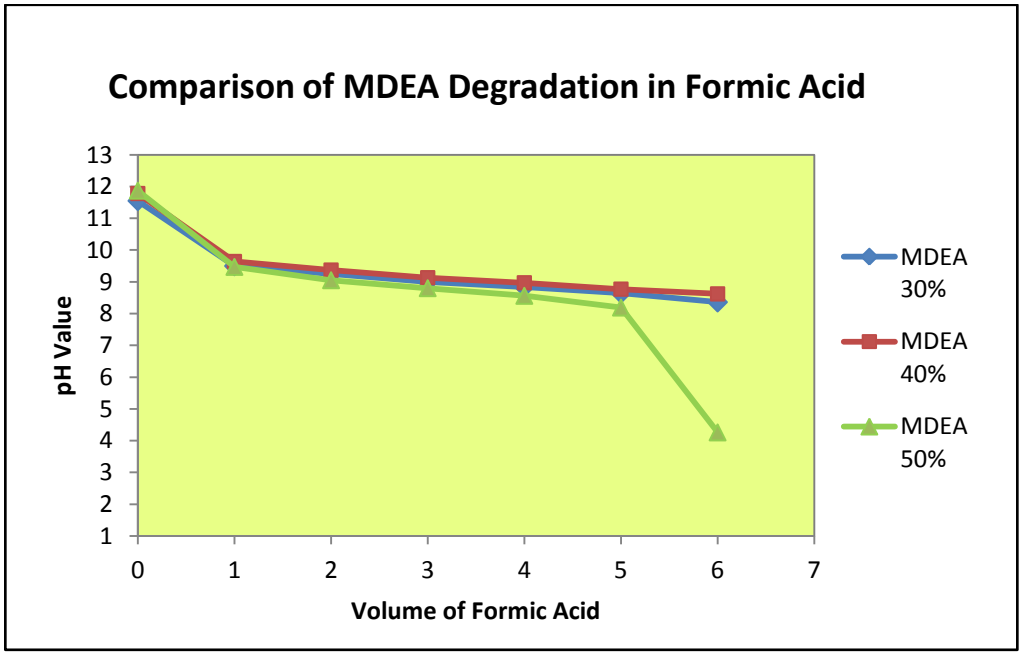

Figure 22: Comparison of MDEA degradation in formic acid at different strengths

4.3 MDEA neutralisation profile

The KOH concentration used is approximately 0.5 N due to the small samples of MDEA that is investigated so that minimal changes in pH can be detected.

Based on the first part of the experiment, the amount of contaminants that shows to be the point of degradation for formic acid is 6ml (6 wt%) and for acetic acid it is 9ml (9 wt%). Since formic acid degrades the solution more than acetic acid another experiment studying the effect of formic acid degradation at 3ml (3 wt%) was performed. The neutralization of KOH with formic acid is represented by the reaction below:

$$\mathbf{KOH + 2HCOOH \rightarrow HCOOK + 2H_2O}$$

The product created in this reaction is potassium formate, a non toxic salt. The basicity ($pK_{b)}$ value of this salt varies from 8-12. According to literatures, at room temperature, which is assumed for this experiment, the pK_b value is 10.25.

The neutralization of KOH with acetic acid is represented by the reaction below:

$$\mathbf{KOH + 2CH_3COOH \rightarrow CH_3COOK + 2H_2O}$$

Potassium acetate is a white deliquescent crystalline powder. According to literatures, the acidity (pK_a) ranges from 3.8 to 5.8 at room temperature which is assumed the case for this experiment.

Using the linear regression equation, the amount of KOH necessary to neutralize the contaminants for formic acid and acetic acid respectively at different concentration is tabulated in the table below:

Table 2: Amount of KOH to neutralize the contaminated MDEA solution

Type of Acid	**Formic Acid**		**Acetic Acid**
Amount of KOH necessary to neutralize MDEA (ml)	**3ml**	**6ml**	**9ml**
30%	2.79	10.97	22.45
40%	10.57	26.44	37.2
50%	12.01	25.87	26.32

Using the data above, the Total Acid Number (TAN) can be calculated. This would give more perspective as to how much acid there was in the original solution and how much KOH it took to neutralize it.

Table 3: Total Acid Number

Type of Acid	**Formic Acid**		**Acetic Acid**
TAN(mgKOH/g)	**3ml**	**6ml**	**9ml**
30%	4.96	11.41	15.19
40%	12.56	17.48	18.57
50%	13.47	17.33	16.29

From the table above, we can see that the amount of formate and acetate in this system has a very high acid number. This shows that these contaminants are very corrosive to the amines system. The graphs obtained for this neutralization reaction is as below:

4.3.1 Formic Acid

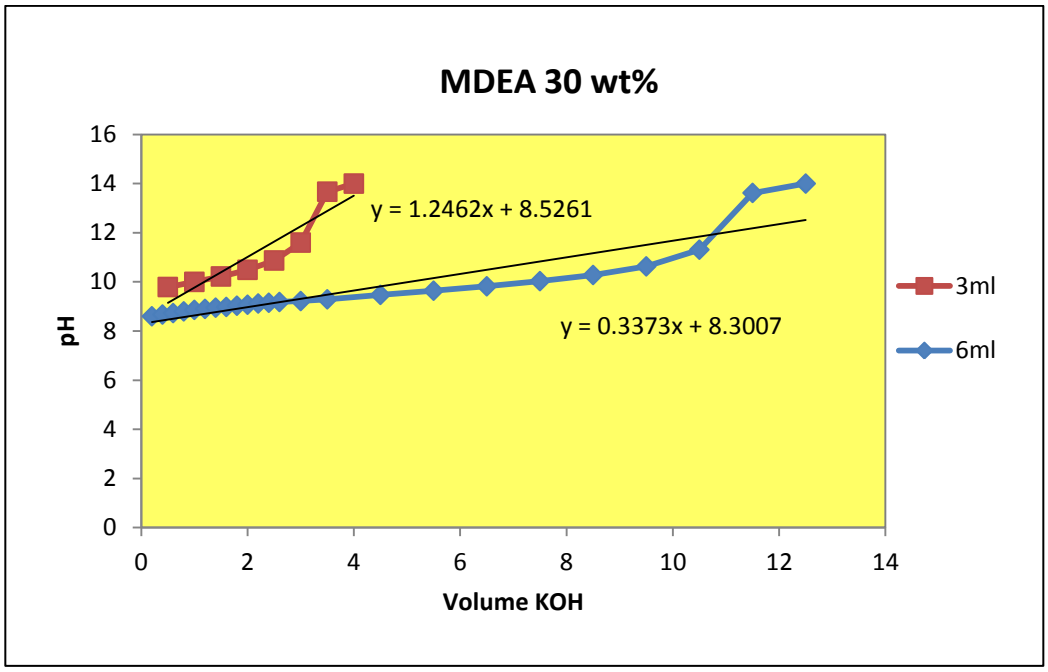

Figure 23: Neutralization profile at 30 wt% with KOH for 3ml and 6ml contaminants

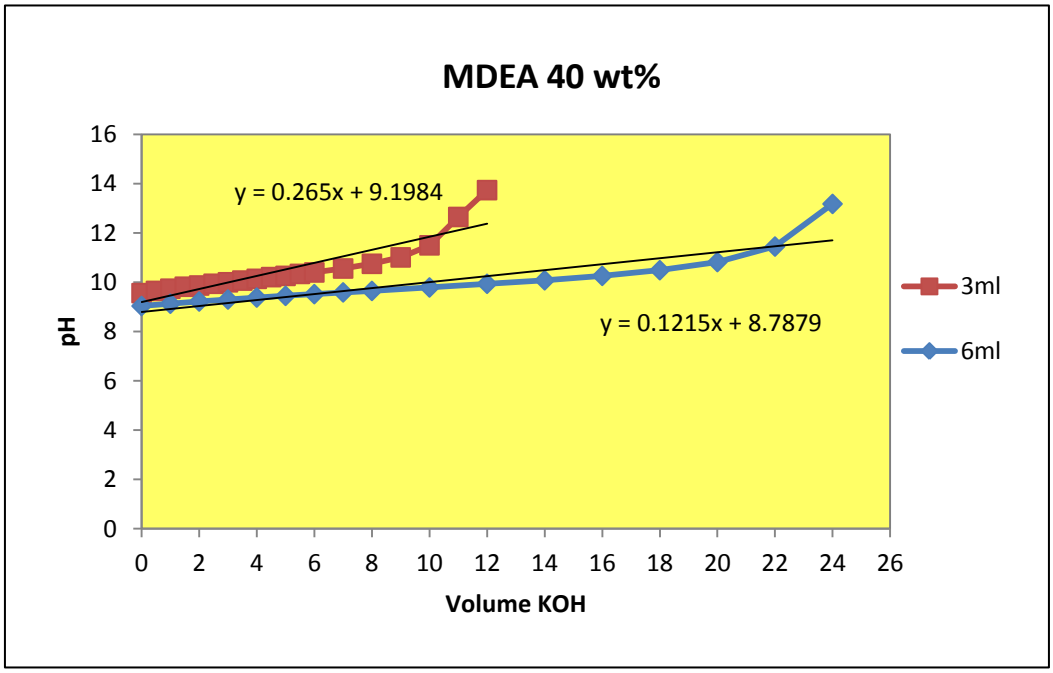

Figure 24: Neutralization profile at 40 wt% with KOH for 3ml and 6ml contaminants

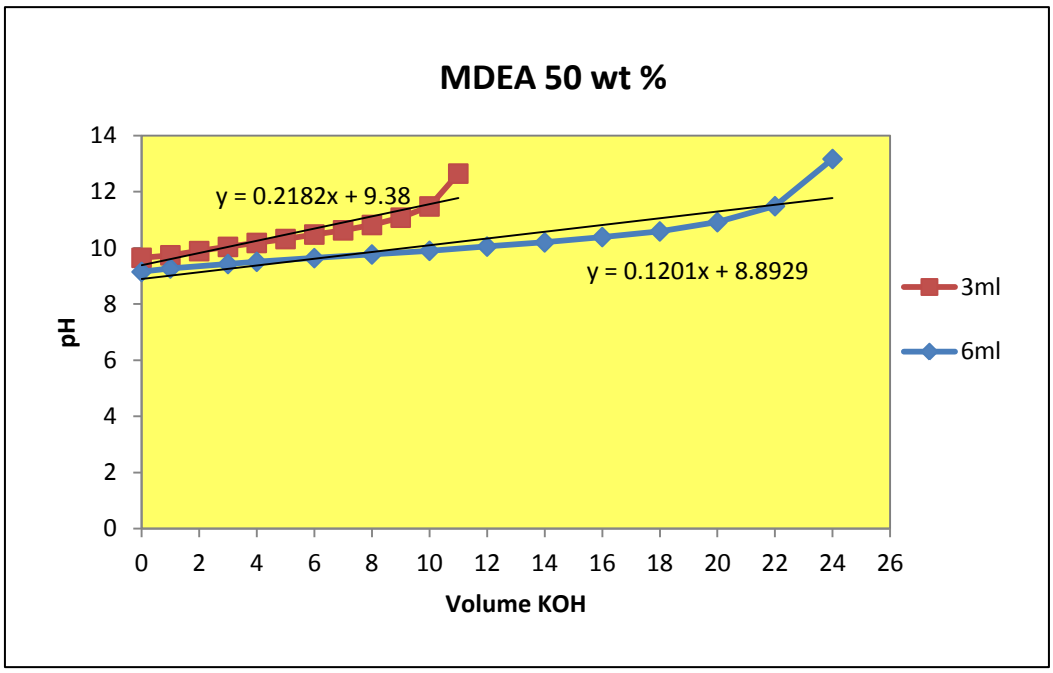

Figure 25: Neutralization profile at 50 wt% with KOH for 3ml and 6ml contaminants

4.3.1 Acetic Acid

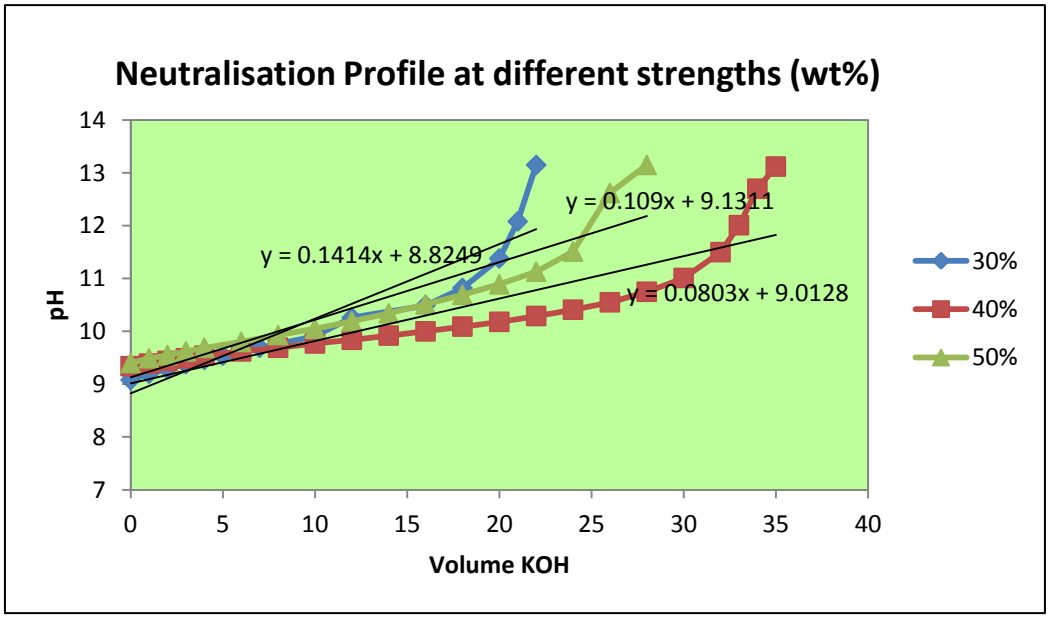

Figure 26: Neutralization profile at 30, 40 & 50 wt% with KOH for 9ml contaminants for acetic acid

Initially when HSS is present in the system, obvious precipitation occurred, the following reactions take place and formed salts.

Formic Acid

$2R'NR_2 + 2HCOOH \rightarrow 2R'NR_2COOH + 2H_2O$

Acetic Acid

$2R'NR_2 + 2CH_3COOH \rightarrow 2R'NR_2\ CH_3COOH + 2H_2O$

The salts formed immediately create a murky white color in the MDEA. After neutralization, it is observed that the solution is no longer murky and all the visible solids are gone. MDEA characteristics are also preserved and the amine is now free to absorb H_2S as it is supposed to.

From the experiments conducted, it is clear that neutralization with KOH is favorable. This is because neutralization changes the corrosive HSS which is formate and acetate to HSAS which is less corrosive to an amine system. From the TAN obtained, KOH effectively neutralized the high amount of acid in the solution.

Therefore, it can be concluded that it is feasible to apply caustic addition to refinery but only as a method to prolong the use of amine in the refinery. From the data obtained the MDEA concentration that is above 30% and less than 50% seems to be the best concentration against contaminants in the system. The higher the concentration of amine, the higher the foaming tendencies and becomes somewhat more vulnerable to degradation incomparable to its strength.

CHAPTER 5

CONCLUSION

This study is done to analyze the effects of neutralization on waste MDEA characteristics. The objectives of this study are achieved. The byproduct (HSAS) which are potassium acetate and potassium formate produced in this neutralization is more harmless than the HSS (formate and acetate) before neutralization. MDEA characteristics and basicity is also retained after neutralization. KOH addition to neutralize HSS is therefore suitable as a short term measure of purging the amine system. It is recommended to be added after the amine has gone through the regenerator to prevent the KOH from neutralizing H_2S instead. From the experiment conducted, the higher the amine concentration the higher the foaming tendencies. However, in an amine system, a higher concentration of amine would help reduce operating cost. The most optimum MDEA strength is 40 wt% according to the data obtained. Neutralization with KOH is deemed feasible for application in an amine gas treating plant.

CHAPTER 6

RECOMMENDATIONS

The recommendations for this project are:

1. MDEA at other strengths (wt%) such as 25,35,45 and 55% should be investigated
2. The use of a round tipped without casing electrode for the pH meter

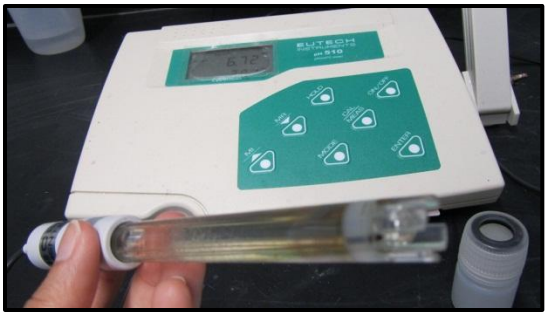

Figure 27: Round tipped electrode with casing makes it difficult to clean and errors in pH reading due to contamination may occur

3. Calculation of H_2S loading for more qualitative measure
4. Calculation of undissociated acid to determine the amount of acid present before neutralization because acid dissociation equilibrium constant is a measure of the strengths of acid.

REFERENCES

[1] Lewis, Richard J. Sr. (2007), Hawley's Condensed Chemical Dictionary, 15th Edition, John Wiley & Sons.

[2] Clark J. (2010), Aliphatic Amines, http://www.chemguide.co.uk , 27 August 2010.

[3] Mathhey J. (2010), Amines Production Technology, http://www.jmcatalysts.com, 27 August 2010.

[4] Nave, C. R. (2010), Amines, http://hyperphysics.phy-astr.gsu.edu/hbase/organic/amine.html, 22 August 2010.

[5] Haws R. (2001), Contaminants in Amine Gas Treating, http://www.reclaim.com/site/referencedocs/comtaminents_in_amine_gas_treating.pdf, 20 August 2010.

[6] Study of MDEA Characteristics through Neutralisation with Caustic and Soda Ash *done for* Engen Refinery, 2010

[7] H.J. Liu and J.W. Dean, (1995), Neutralisation Technology to Reduce Corrosion from Heat Stable Amine Salts, http://www.dow.com/PublishedLiterature/dh_0039, 23 August 2010.

[8] Pohl, W. and Menzel, J. (1997), Process for purifying an aqueous MDEA solution, http://www.freepatentsonline.com/5607594.html, 24 August 2010.

[9] Rooney, Peter C. (1998), Amine heat stable salt neutralization having reduced solids, http://www.wipo.int/pctdb/en/wo.jsp?wo=1998032519, 24 August 2010.

[10] Amines gas treating, http://en.citizendium.org/wiki/Amine_gas_treating, 23 August 2010

[11] Amines, http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/amine1.htm, 20 August 2010.

[12] From Website, DOW Specialty Amines - Typical Physical Properties of DEEA, MDEA, NMEA, http://www.dow.com/amines/prod/tpp_alk.htm, 16 September 2010.

[13] Bullin, Jerry A. (2006), Selective Absorption Using Amines, http://www.bre.com, 20 September 2010.

[14] From Website, MDEA: Proven Technology for Gas Treating Systems, http://www.arkema-inc.com, 20 October 2010.

[15] From Website, Theories of Acids and Bases, http://www.chemguide.co.uk/physical/acidbaseeqia/theories, 29 October 2010.

[16] From Website, Strong and Weak Acids and Bases, http://www.sky-web.pwp.blueyonder.co.uk, 29 October 2010.

[17] From Website, ARKEMA. MDEA, Proven Technology for Gas Treating Systems, www.e-OrganicChemicals.com, 11 June 2011

[18] From Website, Helmenstine, A. M. (2011). About.com Chemistry: http://chemistry.about.com/od/workedchemistryproblems/a/normality-calculation.htm, 10th August 2011

[19] From Website (2002-2005). GraphPad Software: http://www.graphpad.com/quickcalcs/Molarityform.cfm, 15th August 2011

[20] From Website (2000), from Equillibrium: Acid Dissociation Equillibrium Constant: http://library.thinkquest.org/C006669/data/Chem/equilibrium/ka.html, 17th August 2011

[21] From Website, Qualitative measurement of Acids and Bases: http://research.cm.utexas.edu/nbauld/teach/acidsbases.html#ph, 18th August 2011

[22] From Website, Francis, E. (2003). Weight Percent: http://dl.clackamas.edu/ch105-04/weight.htm, 18th August 2011

APPENDIX

Appendix I: Water analysis report

WATER ANALYSIS REPORT

4000110929 Sampled: 28-JAN-2010

ENGEN PETROLEUM LIMITED Reported: 16-FEB-2010

465 TARA ROAD Field Rep: Gabriel, Chukwuka

Wentworth-Durban 90335083

SOUTH AFRICA 4052

	LEAN AMINE II U0209061		LEAN AMINE III U0209062
Sulphur, Total, as SO_4, ppm	9130		2020
Sulphate as SO_4, ppm	342		< 125
Chloride, as Cl, ppm	< 125		48
Calcium Hardness, Total as $CaCO_3$, ppm	7.7		7.0
Magnesium Hardness, Total as $CaCO_3$, ppm	< 5		< 4.9
Copper, Total, as Cu, ppm	< 0.5		< 0.49
Iron, Total, as Fe, ppm	15.4	6.7	
Sodium, as Na, ppm	417		63
Potassium, as K, ppm	24	6.2	
Manganese, Total as Mn, ppm	1.1		< 0.1

Phosphorus, Total as PO_4, ppm	< 5	< 5	
Thiosulphate as S_2O_3, ppm	501	116	
Thiocyanate, as SCN, ppm	4620	642	
Oxalate, as C_2O_4, ppm	< 10		< 10
Chromium, Total, as Cr, ppm	4.4		0.96

Peter Geuns, Laboratory Supervisor

WATER ANALYSIS REPORT

4000110929

ENGEN PETROLEUM LIMITED

465 TARA ROAD

Wentworth-Durban

SOUTH AFRICA 4052

Sampled: 28-JAN-2010

Reported: 16-FEB-2010

Field Rep: Gabriel, Chukwuka

90335083

	LEAN AMINE II U0209061	LEAN AMINE III U0209062
Nickel, Total, as Ni, ppm	0.12	0.10
Total Acid Gas, as w/w % CO_2	2.1	0.3
Acetic Acid, as $C_2H_4O_2$, ppm	755	455
Butyric Acid, as $C_4H_8O_2$, ppm	< 50	< 50
Formic Acid, as CH_2O_2, ppm	17900	1710
Propionic Acid, as $C_3H_6O_2$, ppm	142	< 50
Glycolic Acid, as $C_2H_4O_3$, ppm	614	68
Methyldiethanolamine %	39	24
Heat Stable Salts, % MDEA	5.6	0.60
H_2S Loading, mol H_2S/mol Amine	0.011	< 0.01

Peter Geuns, Laboratory Supervisor

Appendix II: Experiment results

A. MDEA characteristics at different strengths after HSS addition

Table A1: MDEA at 30% strength

Volume	pH	
	Acetic acid	Formic acid
0	11.55	11.55
1	9.82	9.5
2	9.53	9.25
3	9.33	9
4	9.17	8.84
5	9.01	8.64
6	8.82	8.36
7	8.71	8.02
8	8.56	7.05
9	8.4	4.4
10	8.2	4.06
11	7.89	
12	7.4	
15	5.13	
20	4.57	

Table A2: MDEA at 40% strength

Volume	pH	
	Acetic acid	Formic acid
0	11.78	11.78
1	10.04	9.64
2	9.72	9.37
3	9.5	9.13
4	9.37	8.97
5	9.24	8.77
6	9.13	8.62
7	9.02	8.48
8	8.91	8.3
9	8.8	7.96
10	8.69	7.52
11	8.46	4.96

12	8.4	
15	7.63	
17	5.64	
20	4.95	

Table A3: MDEA at 50% strength

Volume	pH	
	Acetic acid	Formic acid
0	11.87	11.87
1	9.97	9.47
2	9.64	9.05
3	9.46	8.8
4	9.25	8.56
5	9.1	8.19
6	8.81	4.26
7	8.62	
8	8.36	
9	7.77	
10	6.2	
11	5.44	
12	5.21	
13	4.82	
20	4.53	

B. MDEA neutralisation profile

Table B1: MDEA at 30% strength with 3ml Formic Acid

Volume KOH	pH
0.5	9.79
1	10
1.5	10.22
2	10.49
2.5	10.87
3	11.6
3.5	13.67
4	14

Table B2: MDEA at 30% strength with 6ml Formic Acid

Volume KOH	pH
0	8.5
0.2	8.6
0.4	8.67
0.6	8.73
0.8	8.8
1	8.86
1.2	8.9
1.4	8.95
1.6	8.98
1.8	9.03
2	9.07
2.2	9.12
2.4	9.15
2.6	9.18
3	9.22
3.5	9.29
4.5	9.47
5.5	9.64
6.5	9.82
7.5	10.03
8.5	10.28
9.5	10.63
10.5	11.31
11.5	13.62
12.5	14

Table B3: MDEA at 40% strength with 3ml Formic Acid

Volume KOH	pH
0	9.04
1	9.13
2	9.22
3	9.3
4	9.38
5	9.45
6	9.52
7	9.59
8	9.65
10	9.79

12	9.94
14	10.08
16	10.26
18	10.49
20	10.82
22	11.45
24	13.18

Table B4: MDEA at 40% strength with 6ml Formic Acid

Volume KOH	**pH**
0	9.04
1	9.13
2	9.22
3	9.3
4	9.38
5	9.45
6	9.52
7	9.59
8	9.65
10	9.79
12	9.94
14	10.08
16	10.26
18	10.49
20	10.82
22	11.45
24	13.18

Table B5: MDEA at 50% strength with 3ml Formic Acid

Volume KOH	pH
0	9.65
1	9.74
2	9.89
3	10.04
4	10.18
5	10.32
6	10.48
7	10.63
8	10.82

9	11.08
10	11.48
11	12.65

Table B6: MDEA at 50% strength with 6ml Formic Acid

Volume KOH	**pH**
0	9.15
1	9.27
3	9.43
4	9.51
6	9.64
8	9.77
10	9.9
12	10.05
14	10.2
16	10.39
18	10.59
20	10.92
22	11.49
24	13.17

Table B7: MDEA at 30% strength with 9ml Acetic Acid

Volume KOH	**pH**
0	9.08
1	9.2
2	9.29
3	9.38
4	9.46
5	9.54
6	9.62
7	9.69
8	9.76
10	9.91
12	10.26
16	10.49
18	10.82
20	11.38
21	12.08
22	13.15

Table B8: MDEA at 40% strength with 9ml Acetic Acid

Volume KOH	pH
0	9.34
1	9.39
2	9.44
3	9.49
4	9.54
6	9.62
8	9.69
10	9.77
12	9.84
14	9.92
16	10
18	10.09
20	10.18
22	10.29
24	10.41
26	10.55
28	10.75
30	11.01
32	11.5
33	12.01
34	12.7
35	13.12

Table B9: MDEA at 50% strength with 9ml Acetic Acid

Volume KOH	pH
0	9.4
1	9.49
2	9.55
3	9.62
4	9.69
6	9.8
8	9.93
10	10.05
12	10.19
14	10.34
16	10.51
18	10.69

20	10.89
22	11.13
24	11.51
26	12.62
28	13.15